THE CHANGE OF MOLECULAR KINETIC ENERGY INTO MOLECULAR POTENTIAL ENERGY: THE ENTROPY PRINCIPLE AND MOLECULAR ASSOCIATION

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Communicated by J. Stieglitz, September 16, 1919

My work on the orientation of molecules in the surfaces of liquids (Langmuir has also worked on orientation) has led to the recognition of a remarkable new principle or law concerning the change of molecular kinetic energy into molecular potential energy. None of the kinetic relations already found in the very simple case where gases alone are involved, have been found to be as exact as the laws of thermodynamics, since by their very nature such relations are affected by many extraneous complicating factors. It need not then be surprising if similar relations involving the much more complicated and hitherto obscure kinetic phenomena of the liquid and the solid states should prove to be approximate rather than exact. Thus it is well known that Raoult's law concerning the kinetics of the vaporization of the various components in a solution, is exact only in an extremely limited range, that is when the components are practically alike with respect to cohesion[1] or with respect to the electromagnetic fields surrounding their molecules.[2] It is, therefore, somewhat startling to find that my new relation or law is, in one of its forms, much more generally applicable than Raoult's law, at least if the data at present accepted in this connection are as exact as they are supposed to be.

The new principle or law will first be stated in one of its special forms as follows: *Whenever a molecule moves from the interior of a liquid into the surface in such a way as to form a new surface, the average amount of its*

kinetic energy which is converted into potential energy is equal to 144% of the mean translational kinetic energy of a gas molecule at the same temperature. This indicates that in general only the faster moving molecules possess sufficient kinetic energy to carry them into the surface. All known plane surfaces have a positive free surface energy, that is the molecular potential energy in a plane surface in which the above principle holds is always greater than 144% of the mean kinetic energy of its molecules.

Application to the theory of surfaces.—As has been indicated in the last paragraph the molecules in a surface possess potential energy by virtue of their position. When a new surface is formed the principle given above indicates that a definite portion of this potential energy results from a tranformation of the kinetic energy of molecular motion into the potential form, and that the amount of energy supplied in this form depends only upon the temperature; and is proportional to the temperature. *The free energy of the surface is simply the difference between the total energy, which depends upon the structure of the surface, and the latent heat of the surface which is conditioned by the above law.* It is easy to see why, on this basis, the surface tension or the free surface energy decreases with the temperature. The total surface energy is approximately constant while the temperature is varied, provided the critical temperature is not too closely approached, which is the condition also for the application of the new principle since the surface film thickens as the critical temperature is neared. Since the contribution of the kinetic energy of molecular motion to this total energy is proportional to the absolute temperature, the free surface energy must decrease with the temperature.

The entropy law.—According to Lunn[3] heat has two measurable aspects, energy and entropy. The first law of thermodynamics relates to heat changes in which energy is, but entropy is not, conserved. The second law considers heat changes in which energy in the form of heat alone is not, but entropy is, conserved. The principle discovered by me has been stated above in terms of energy but it may be much more simply stated in terms of entropy as follows: *Whenever a molecule moves from the interior of a liquid into its surface in such a way as to form a part of a new surface, the entropy of surface formation is not only independent of the nature of the molecule, but is also independent of the temperature.* The numerical value of this entropy is 2.96×10^{-16} ergs per degree per molecule.

This entropy is not the ordinary thermodynamic entropy but is about

15% less than the thermodynamic entropy calculated for the area occupied by one molecule. The entropy which corresponds to the value given above is that which is calculated for the area of surface occupied by one molecule on the supposition that the arrangement of the molecules is such as to give approximately the same number of molecules in the surface as if it were built up on the plan of a cubic lattice, and the area for which the entropy is calculated is always that occupied by one molecule no matter what the temperature may be. The difference between these two entropies will be discussed later, but it is not essential *since either of them shows the constancy required by the relation under discussion.* When the extent of the molecular orientation in the surface is known it should be taken into account.

Relation of the entropy law to molecular association.—Although the entropy principle presented in this paper was discovered by the writer not more than a few years ago, a number of empirical relations which involve its validity without its recognition by their discoverers, have been well known for many years. The empirical relation directly related to the form of the entropy principle already given, is known as the law of Eötvös,[4] Ramsay, and Shields.[5] While a part of this relation was developed by Eötvös from a special form of the theorem of corresponding states, in its final form, as given by Ramsay and Shields, it may be considered as purely empirical, and it is this latter form which is given by the entropy principle. Indeed, though it does not seem to have been recognized by them, Ramsay and Shields relation gives the entropy of a surface, though in very peculiar units, and also the entropy expressed by it is not the ordinary thermodynamic entropy.

The thermodynamic entropy may be expressed in ergs per degree per square centimeter, or in other units. The Ramsay and Shields relation may be expressed in terms of entropy, if a somewhat unusual unit is used for the measurement of the area, in the following terms: *The entropy of the surface of a liquid is 2.12 ergs per degree for an area which is equal to the area of one face of a cube which contains one gram molecule of the liquid.* Since the volume of such a cube varies with the temperature, the area to which the entropy is referred also varies with the temperature.

The value in the use of such a peculiar system does not lie in the use of the same number of molecules in the box in every case, but in the use of the area of one face of the box, the inherent idea being that in this way the same number of molecules in the surface are obtained in every case when the molecules in the surface are counted by considering that their complexity in the surface to be the same as that inside the liquid.

It is obvious that this depends either upon the approximation to a cubic lattice arrangement, or to a similarity in the surface arrangement in every case. It is therefore to be expected that the relation would not hold in any case where the molecular orientation in the surface is such as to cause a deviation from such similarity.

While the normal value for the fraction of the molecular kinetic energy which is converted into the potential form is 144% of the mean molecular kinetic energy, which corresponds to a surface entropy of 2.96×10^{-16} ergs per molecule, and while what have been usually termed normal or unassociated liquids give these values very closely, certain liquids have been found for which the entropy value is lower. Thus the alcohols, organic acids, and water, give at ordinary temperatures not far from one-half the normal values (one-third in the case of water), but as the temperature increases, even for such liquids the entropy increases and approaches the normal value. Such results as these are easily explained on the basis of the assumption made by Ramsay and Shields and their followers in the association school, who consider that at low temperatures the molecules in such liquids are associated into larger groups than correspond to the formula weight, but that the association decreases as the temperature increases.

Criticisms of the Ramsay-Shields method of determining molecular association.—Certain sweeping criticisms of the Ramsay-Shields method of calculating the degree of molecular association which have been made, I consider to have no validity. On the other hand objections might be raised which seem not to have occurred to the workers in this field. The most sweeping criticism of the method, which has been expressed many times, is that since it is a "surface tension method it gives no true indication of the molecular state of the liquid as a whole." From this view-point it is considered that it is not the association in the liquid, but the association in the surface, which is calculated by this method. With this criticism I disagree most strongly, for if Ramsay and Shields have calculated any association at all it is not that in the surface, but that which exists in the body of the liquid, as seems to me apparent from the entropy principle, for the kinetic energy which is converted into the potential energy of the surface is the molecular kinetic energy of the molecules just before they move into the surface.

A second criticism which has been made is that very complex molecules, particularly those which contain several, paraffin chains such as tripalmatin and tristearin, give much too large values of the Ramsay-Shields constant. I have found, however, that a very great reduction

in the value of the constant is obtained if the molecular orientation in the surface is taken into consideration, which was not done by Ramsay and Shields. While the values which are thus obtained are still somewhat larger than the normal, it must be remembered that such complex molecules may vibrate in parts, which might very well give larger amounts of kinetic energy available for transformation into potential energy.

While Ramsay and Shields evidently did not see at all the important theoretical basis for their method it is nevertheless true that their equation involved the entropy of formation of the surface, and therefore kept closer to this basis than the very great number of supposedly improved equations which have been developed from it.

In so far as the experimental results for the temperature coefficients of free surface energy as determined by Ramsay and Shields can be trusted, our calculations show that the normal value of the surface entropy per degree per molecule is very close to the normal value $(2.96 \times 10^{-16}$ ergs) for the following substances over a wide temperature range: benzene, carbon tetrachloride, ethyl acetate, ethyl ether, methyl formate, and chlorobenzene. The results of Baly and Donnan give 2.8×10^{-16} for liquid nitrogen, and 2.75×10^{-16} for liquid oxygen.

On the other hand the values for argon (1.6×10^{-16}) and for mercury (1.5×10^{-16}), though not so well established experimentally, are not very much above 50% of the normal values, and the work of Jaeger indicates that molten salts also give low values. Unfortunately the data for argon were obtained over such a small temperature range that the entropy obtained may be very much in error. In the case of mercury and the molten salts, those who belong to the extreme association school would assume that the entire deviation is due to molecular association, but I am not at all convinced that the association is at all definite, especially since our present knowledge of the structure of metals and salts indicates that there may not be such a thing as a definite molecular weight in any case. This subject will be treated more comprehensively in a later paper.

A general form of the entropy principle.—In the preceding paragraph I have presented the entropy principle in its relation to the formation of surfaces, in which case it seems to hold remarkably well. Possibly it is only in the formation of surfaces that such a relation will be found to hold with exactness, as the following reasoning will indicate. In the formation of a surface the *total* energy converted into molecular potential energy must be of such a magnitude as to overcome the

cohesive forces to the extent which is necessary in the formation of the surface. However, as has already been stated, all of this energy does not come from the molecular motion, but a part of it is introduced by the action of an external force, which does the work necessary to produce what is called the free energy of the surface. The energy which is not supplied by the molecular motion, must be supplied in the form of work, so the amount of energy supplied by the molecular motion is not uniquely determined by the cohesive forces. When a liquid vaporizes in an ordinary experiment, the *whole* of the energy necessary for the separation of the molecules against the cohesive forces, is supplied by the energy of molecular motion, except for the amount which may be supplied by changes in the potential energy of the molecules themselves, and the latter is probably not a very important factor. It is obvious that the contribution of the molecular motion to the formation of a surface may be largely independent of the cohesive forces involved, and this is made probable by the validity of the entropy principle in this case. The cohesion enters so directly into the heat of vaporization that it would seem doubtful if for it the entropy principle would hold. It would seem surprising, too, if the principle should hold for melting, for sublimation, or for sublimation combined with dissociation.

Nevertheless, a study of the literature shows that while the entropy principle itself has hitherto remained unrecognized, there are a number of empirical relations, which if they hold, involve the validity of a much more general entropy principle. Without discussing to what extent I believe such a principle is valid, I will state it in two different forms as the theoretical basis of all of these empirical relations. In order to give this statement I will define a *region* as a phase, surface, or interface. *When in a system consisting of one component, a molecule moves from one region into another, the average molecular kinetic energy which is converted into the form of molecular potential energy depends in general only on the change of state, that is on the region from which the molecule comes and the one into which it goes, provided* that when a vapor phase is involved one condition which enters is the state of the vapor with reference to one variable. According to Trouton this condition is that the pressure of the vapor shall be the same in all cases, and this has been modified by Hildebrand, with an increase in accuracy, to the condition that the molecular concentration of the vapor phase shall be the same in all cases. In the second form, the principle states that the *entropy* of the change depends only on the change of state, and not on the individual nature of the molecules. In the application of this

principle the surface of a metal is not considered as a region of the same class as the surface of water or an organic liquid, since the characteristics of the two regions are quite unlike.

Corresponding to the various empirical relations the following 'normal' values of the entropy may be given:

Entropy in ergs per degree per molecule ×10¹⁶ → $\times 10^{16}$

1. Liquid to surface.. 2.96
2. Liquid to vapor at the special concentration of:
      c = 0.00507 mols per liter..18.8
      c = 0.0127 mols per liter...16.7
      c = 0.0201 mols per liter...15.7
      (These values become less accurate as the concentration of the vapor increases.)
3. Solid to vapor at the melting point....................................21.0
4. Solid to liquid.. 9.0
5. Solids dissociate to 760 mm. vapor pressure............................22.0

Of these the first is the most exact, the second holds moderately well under the conditions imposed, and the fourth, as might be expected, is one of the least accurate. Walden's rule is that the molar heat of fusion divided by the temperature is equal to 13.5 calories per degree for normal substances, or the molar entropy of fusion has the given value. This rule Walden[7] found to hold for a large number of organic substances. When the data did not correspond with what should be obtained according to the rule, Walden assumed that it still remains valid, but that the molecular weight is different from that given by the formula. However it is evident that this explanation is not sufficient to account for all of the deviations which exist.

At my request Mr. L. E. Roberts has studied practically all of the available data on the entropy of melting, and has found the general relations which hold. One of the greatest obstacles in this connection is that the data are in many cases extremely inaccurate. They indicate that the *latent heat of melting* of a metallic element which crystallizes in the regular system, *increases as the melting point rises*, and the entropy averages about 2.2 calories per gram atom per degree.[8] The salts show a somewhat similar relation, and at the same time there seems to be a general increase in the entropy of fusion with the number of gram atoms in the formula weight of the salt. There is a great deal of irregularity, but for the halogen salts the entropy is of the order of 2.2 calories per degree per gram atom, or about the same value as is found for the metals.[9] Hydrogen, hydroxides and water of crystallization are represented by lower values. Thus the entropy of fusion of the hydroxides of sodium, potassium, rubidium, and caesium, is about 2.8 calories per

degree per gram molecule. On turning to molecular compounds such as ammonia and carbon dioxide it is found that the entropy of fusion is 9.3 for the former and 8.9 for the latter, while for benzene the value is 8.3. Corresponding to Walden's rule a large number of organic compounds have entropies of fusion between 12 and 14 calories per degree, while many of the substances with smaller entropies of fusion possess other properties characteristic of associated liquids when they are in the liquid state. As might be expected substances with very complex formulae give high values, the increase with molecular complexity being very distinct. Thus with stearic acid ($C_1H_{36}O_2$) the value rises to 40, while the acid with two carbon atoms has an entropy of only 9.5, with nine carbon atoms of 10.5, while in the case of the 12 carbon atom acid the value rises to 27.

It is thus to be seen that the entropy is a very important function in a study of the transfer of molecules from one region to another, and that *in general the price which a molecule has to pay in terms of energy in order to undergo any certain change, increases with the temperature* or the molecules pay in proportion to their wealth with respect to energy. There is also an increase in this energy price whenever the complexity of the molecules increases sufficiently. The price in terms of entropy is much more constant than the price in terms of energy, and in this sense there is an analogy to the action of a Carnot engine.

It is believed that the point of view presented in abstract in this short paper will greatly change the present attitude in regard to the determination of molecular association in liquids, and it is possible that it may be of importance in a study of the general subject of the partition of energy, as well as in changes of kinetic into potential energy.[10]

The complete paper of which this is a part will be presented to the *Journal of the American Chemical Society* by Mr. L. E. Roberts and the writer, for publication in a later issue.

[1] *J. Amer. Chem. Soc., Easton, Pa.*, **38**, 1916, (1452).

[2] *Ibid.*, **41**, 1919, (970–92). PROCEEDINGS, May, 1919.

[3] *Physic. Rev.*, July, 1919.

[4] *Leipzig, Ann. Physik*, **27**, 1886, (452).

[5] *London, Phil. Trans. Roy. Soc.*, 184A, 1893, (647), *Zs. Physik. Chem., Leipsig*, **12**, 1893, (647).

[6] *J. Amer. Chem. Soc.*, **37**, 1915, (975).

[7] *Zs. Elektrochem.*, **14**, 1908, (715).

[8] Crompton, *J. Chem. Soc.*, **67**, 1895, (315–327). T. W. Richards, *J. Franklin Institute*, 1902.

[9] Wayling, *Phil. Mag.*, **37**, 1919, (495).

[10] Since this paper was submitted I have received a copy of a paper presented to the Société Française de Physique by M. J. Duclaux on June 6, 1919. He believes that there are quantities of energy of magnitude 6.6×10^{-16} ergs.